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**Notes:**

1. Untranslatable words are replaced with asterisks (\* \*\*).
2. Texts in the figures are not translated and shown as fig.

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**CLAIM + DETAILED DESCRIPTION**

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**[Claim(s)]**

[Claim 1]A manufacturing method of an isocyanurate group content polyisocyanate which is a manufacturing method which performs an isocyanuration reaction for organic diisocyanate under existence of a catalyst and a co-catalyst, and is characterized by using ascorbic acid for a co-catalyst.

[Claim 2]A manufacturing method of an isocyanurate group content polyisocyanate which is a manufacturing method which performs a urethane-ized reaction and an isocyanuration reaction for organic diisocyanate and a polyol in parallel under existence of a catalyst and a co-catalyst, and is characterized by using ascorbic acid for a co-catalyst.

[Claim 3]A manufacturing method of the isocyanurate group content polyisocyanate according to claim 1 or 2, wherein organic diisocyanate is hexamethylene di-isocyanate.

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**[Detailed Description of the Invention]**

[0001]

[Field of the Invention]This invention relates to the manufacturing method of an isocyanurate group content polyisocyanate.

[0002]

[Description of the Prior Art]Since what is obtained from an isocyanurate group content polyisocyanate, especially hexamethylene di-isocyanate is excellent in weatherability, chemical resistance, abrasion resistance, etc., it is used for a coating material, ink, adhesives, etc. In the fields the object for automobile repair, for the construction exterior, etc., it is in use especially as a coating material.

[0003]An isocyanurate group content polyisocyanate has many things containing a reaction catalyst, a co-catalyst, a reaction stopper, etc., therefore there are problems, such as coloring

and the body up.

[0004] Various examination is made in order to improve this point. For example, it is examined that organic phosphite is used for JP,S61-129173,A as a co-catalyst. It is examined that the quencher (reaction stopper) which has a urea derivation group and a thiourea derivation group is used for JP,H2-110123,A. It is examined that a common No. 138343 [ 07 to ] gazette uses peroxy carboxylic acid for a reaction stopper.

[0005]

[Problem to be solved by the invention] In an isocyanuration reaction, the purpose of this invention is to use a specific co-catalyst, and is providing the manufacturing method of the isocyanurate group content polyisocyanate which was excellent in productivity.

[0006]

[Means for solving problem] As a result of carrying out research examination, by using ascorbic acid for the co-catalyst of an isocyanuration reaction, this invention persons find out that above-mentioned SUBJECT is solvable, and came to complete this invention.

[0007] That is, this invention is shown in the following (1) - (3).

(1) A manufacturing method of the isocyanurate group content polyisocyanate which is a manufacturing method which performs an isocyanuration reaction for organic diisocyanate under existence of a catalyst and a co-catalyst, and is characterized by a co-catalyst containing ascorbic acid.

[0008] (2) A manufacturing method of the isocyanurate group content polyisocyanate which is a manufacturing method which performs a urethane-ized reaction and an isocyanuration reaction for organic diisocyanate and a polyol in parallel under existence of a catalyst and a co-catalyst, and is characterized by a co-catalyst containing ascorbic acid.

[0009] (3) A manufacturing method of the above (1) or the isocyanurate group content polyisocyanate of (2), wherein organic diisocyanate is hexamethylene di-isocyanate.

[0010] The raw material etc. which are first used for this invention are described. This invention uses ascorbic acid for the co-catalyst of an isocyanuration reaction. Since the toxicity over a human body is dramatically small as compared with phenol and the organic phosphite for which ascorbic acid is used as a usual co-catalyst, work environment of this invention is good. When this ascorbic acid was used as a co-catalyst of an isocyanuration reaction, it became clear that the rate of reaction of isocyanuration increased. For this reason, the manufacturing method of the isocyanurate group content polyisocyanate excellent in productivity can be provided. Since the solubility of ascorbic acid to organic diisocyanate of a raw material and the isocyanurate group content polyisocyanate of a product is small, it is filtering a resultant and an isocyanurate group content polyisocyanate with few impurities is obtained. Since organic diisocyanate of a raw material is the liquid phase, ascorbic acid of a co-catalyst is solid phase, and the contact time of the co-catalyst of raw material organic diisocyanate is very short, an

isocyanurate group content polyisocyanate with little coloring is obtained. Since it is usually produced by the fermentation industrial target, and ascorbic acid tends to obtain L-ascorbic acid, it is preferred.

[0011] In this invention, a co-catalyst publicly known [ other than ascorbic acid ] as a co-catalyst. For example, phenolic hydroxyl group-containing compound, such as phenol and hydroquinone, Alcoholic hydroxyl group content compounds, such as methanol and ethylene glycol, Epoxy compounds, such as dialkyl tin compounds, such as organophosphate, such as organic phosphite, such as diethyl phosphite, and triethyl phosphate, and dibutyltin dilaurate, and phenyl glycidyl ether, a urethane group content compound, etc. can be used together.

[0012] As for the rate of a mass ratio of ascorbic acid (a) and compound (b)s other than ascorbic acid, (a):(b) = 100:0 - 5:95 are preferred.

[0013] [ as organic diisocyanate used for this invention ] 4 and 4'-diphenylmethane diisocyanate, 2, 4'-diphenylmethane diisocyanate, 2 and 2'-diphenylmethane diisocyanate, 2, 4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenyletherdiisocyanate, 2-nitrodiphenyl-4,4'-diisocyanate, the 2,2'-diphenylpropane- 4, 4'-diisocyanate, The 3,3'-dimethyldiphenylmethane 4, 4'-diisocyanate, 4 and 4'-diphenylpropanediisocyanate, o-phenylene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 1,4-naphthalene diisocyanate, 1,5-naphthalene diisocyanate, Aromatic diisocyanate, such as 3,3'-dimethoxy diphenyl-4,4'-diisocyanate, Tetramethylene di-isocyanate, pentamethylene diisocyanate, hexamethylene di-isocyanate, heptamethylene diisocyanate, octamethylene diisocyanate, dodecamethylene di-isocyanate, Aliphatic series diisocyanate, such as lysine diisocyanate, o-xylenediisocyanate, Aromatic aliphatic series diisocyanate, such as m-xylenediisocyanate, p-xylenediisocyanate, and tetramethyl xylenediisocyanate, One sort or two sorts or more of mixtures, such as isophorone diisocyanate, hydrogenation toluene diisocyanate, hydrogenation diphenylmethane diisocyanate, hydrogenation xylenediisocyanate, and hydrogenation tetramethyl xylenediisocyanate, are mentioned. In this invention, when the polyisocyanate obtained is used as a coating material, and weatherability, plasticity, etc. of a paint film are taken into consideration, aliphatic series diisocyanate is preferred and especially hexamethylene di-isocyanate is preferred.

[0014] When a polyol is used, the polyisocyanate obtained is used as a coating material and film strength etc. are taken into consideration, especially the molecular weight has [ 500 or less ] 450 or less preferred low-molecular polyol. As this low-molecular polyol, ethylene glycol, 1,2-dihydroxypropane, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-dihydroxyhexane, 3-methyl-1,5-pentanediol, neopentyl glycol, 2,2-diethyl- 1,3-propanediol, 2-ethyl-2-n-butyl 1,3-propanediol, 1,8-octanediol, 1,9-nonanediol, diethylene glycol, One sort or two sorts or more of mixtures, such as ethyleneoxide of dipropylene glycol, 1,4-cyclohexane dimethanol, or bisphenol A or a propylene oxide addition product,

trimethylolpropane, glycerol, and pentaerythritol, are mentioned. If compatibility with other resin (base resin), the image clarity of a paint film, etc. are taken into consideration when the polyisocyanate obtained is used as a coating material in this invention, The low-molecular diol which has a side chain alkyl group is preferred, and especially 1,3-butanediol, Neopentyl glycol, 3-methyl-1,5-pentanediol, 2-ethyl-2-n-butyl 1,3-propanediol, and 2-ethyl-2-n-butyl 1,3-propanediol are preferred.

[0015]In this invention, in order to adjust an average functional group number, compatibility, reactivity, etc., a compound of one organic functions may be used together. As a compound of these one organic functions, methanol, ethanol, propanol, Low-molecular monoalcohol, such as 2-ethyl-hexanol and benzyl alcohol, Polymer monoalcohols, such as a methoxy poly (oxyethylene) glycol and ricinoleic acid alkyl ester, Monoisocyanates, such as monoamines, such as ethylamine, diethylamine, a butylamine, and dibutyl amine, a butyl isocyanate, phenyl isocyanate, and a cyclohexyl isocyanate, are mentioned. These may be independent or may be used two or more sorts. A reaction time term of this 1 organic-functions compound may be before an isocyanuration reaction or the back, and what is necessary is just to choose it suitably according to viscosity or a grade of isocyanuration.

[0016][ as an isocyanuration catalyst used for this invention ] Tetramethylammonium hydroxide, tetraethylammonium hydroxide, Tetraalkylammonium hydroxide, such as tetrabutylammonium hydroxide, An acetic acid tetramethylammonium salt, a tetraethylammonium acetate salt, Organic weak acid salts, such as an acetic acid tetrabutylammonium salt, TORIMECHIRU hydroxypropyl ammonium hydroxide, Trimethyl hydroxyethyl ammonium hydroxide, triethyl hydroxypropyl ammonium hydroxide, Trialkyl HIDOROKISHIKIRU ammonium hydroxide, such as triethyl hydroxyethyl ammonium hydroxide, Acetic acid triethyl hydroxypropyl ammonium salt, acetic acid trimethyl hydroxyethyl ammonium salt, The third class amine, such as organic weak acid salts, such as acetic acid triethyl hydroxypropyl ammonium salt and acetic acid triethyl hydroxyethyl ammonium salt, triethylamine, and a triethylene diamine, acetic acid, valeric acid, isovaleric acid, caproic acid, octylic acid, One sort or two sorts or more of mixtures, such as metal salt of alkyl carboxylic acid, such as myristic acid, are mentioned.

[0017]Next, a reaction procedure, reaction conditions, etc. are described. This invention carries out the isocyanuration of the organic diisocyanate under existence of a catalyst and a co-catalyst. Or a urethane-ized reaction and an isocyanuration reaction are performed for organic diisocyanate and a low-molecular polyol in parallel under existence of a catalyst and a co-catalyst.

[0018]That is, when using organic diisocyanate and a low-molecular polyol for a reaction vessel, a low-molecular polyol is taught. As for the raw material temperature at this time, 50 °C or less is preferred. Subsequently, an isocyanuration catalyst and a co-catalyst are taught and

heated and an isocyanuration reaction is performed. It is preferred to heat before the preparation of an isocyanuration catalyst and a co-catalyst, and, as for the temperature in this case, 30-70 °C is preferred. When a low-molecular polyol exists in a system, a urethane-ized reaction will also be performed in parallel. Package preparation, dividing addition, etc. are mentioned as the addition method of an isocyanuration catalyst. In the case of dividing addition, each amounts of catalyst preparations may differ also in equal weight.

[0019]The amount of the isocyanuration catalyst used has the preferred range of 0.001 - 0.5 mass % to organic diisocyanate. 40% or less and also 35% or less of conversion (percentage reduction of an isocyanate group) is desirable. If a reaction progresses too much, it will become easy to gel, and the thing of the shape made into the purpose is no longer obtained. For this reason, reaction conditions, such as reaction temperature, loadings, and the addition method, must be chosen carefully.

[0020]The amount of co-catalyst used has the preferred range of 0.001 - 10 mass % to organic diisocyanate. Although the usual isocyanuration catalyst is uniformly distributed in a system (dissolution), it will distribute in a system without almost dissolving in reaction liquid, since ascorbic acid is water solubility.

[0021]As for temperature of isocyanuration reaction time, 0-90 °C is usually preferred, and it is especially preferred. [ of 30-70 °C ] An inactive solvent of daily use in the bottom of solvent absence, or polyurethane industry, for example, toluene, a reaction, Ketone systems, such as aromatic series, such as xylene, methyl ethyl ketone, and methyl isobutyl ketone, Ester systems, such as ethyl acetate and butyl acetate, propylene-glycol-methyl-ether acetate, With reaction temperature, it can carry out into plasticizers, such as a liquefied polyol or DOP (dioctyl phthalate), if needed under existence of glycol-ether-ester systems, such as diethylene glycol butyl ether acetate and ethyl-3-ethoxy propionate. It is more desirable not to use organic solvents in this invention, if a process after a reaction, etc. are taken into consideration.

[0022]When using a low-molecular polyol, what is called a publicly known urethane-ized catalyst may be used for reaction time. Specifically, organic amine, its salts, etc., such as organometallic compounds, such as dibutyltin dilaurate and dioctyl CHINJI laurate, a triethylene diamine, and triethylamine, are mentioned.

[0023]As for an isocyanuration reaction, it is preferred to inactivate the above-mentioned catalyst using a reaction stopper, and to stop a reaction. As this reaction stopper, alkyl acid phosphate, such as phosphoric acid, phosphorous acid, ethyl phosphorate, and diester phosphate, Organic acid halide, such as organic peroxide, such as acid phosphite, such as phosphorous acid ethyl and diethyl phosphite, sulfur, hydrochloric acid, nitric acid, sulfuric acid, toluenesulfonic acid, toluenesulfonic acid ester, and benzoyl peroxide, and acetic acid chloride, etc. are mentioned. As for the amount of the reaction stopper used, 0.8-2 Eq is preferred to an isocyanuration catalyst.

[0024]When an isocyanuration reaction is completed, it is preferred to filter and remove ascorbic acid, a suspended matter, etc., and also to remove organic diisocyanate of isolation by means, such as extraction and distillation. It is more desirable to remove the organic isocyanate of isolation until the content in a product becomes below one mass each % and also below 0.9 mass each %. The collected organic diisocyanate is used again and can be utilized effectively.

[0025]The viscosity in 25 ° of the isocyanurate group content polyisocyanate obtained by this invention has preferred 500 - 5,000 mPa-s (at the time of 100% of solid content conversion), and especially its 1,000 - 3,000 mPa-s is preferred. An isocyanate group content has preferred 10 - 35 mass % (at the time of 100% of solid content conversion), and its 15 - 30 mass % is especially preferred. As for a color number, three (Gardner) or less are preferred, and two (Gardner) especially or less are preferred.

[0026]Additives, such as an antioxidant, an ultraviolet ray absorbent, a pigment, a color, a solvent, a flame retarder, hydrolysis inhibitor, a lubricant, a plasticizer, a bulking agent, and a storage stabilizer, can be further blended with the polyisocyanate obtained by this invention suitably if needed.

[0027]

[Working example]Although an embodiment and a comparative example explain this invention still in detail, this invention is not limited at all by these. In an embodiment and a comparative example, "mass %" is meant all%."

[0028]993 g and 1,3-BD were taught for HDI, 0.4 g and 0.1g of L-ascorbic acid were taught to the reactor of capacity:2L with embodiment 1 agitator, a thermometer, a nitrogen seal pipe, and a condensor for 3 g and phenol, and nitrogen substitution of the inside of a reactor was carried out. The appearance of mixed liquor was in the state which L-ascorbic acid distributed in the liquid which dissolved raw materials other than L-ascorbic acid. Next, 0.2g of THF solutions (10%) of potassium isovalerate were prepared, and the urethane-ized reaction and the isocyanuration reaction were performed in parallel at 50 ° for 7 hours. Then, 0.02g of phosphoric acid was added, it agitated with reaction temperature for 1 hour, and the reaction was stopped. Reaction liquid was filtered and ascorbic acid was removed. The isocyanate content of this liquid was 32.5%. Subsequently, thin film distillation was carried out at 160 ° and 13.3 Pa, unreacted HDI, phenol, and THF were removed, and the isocyanurate group content polyisocyanate P-1 was obtained. As for P-1, 20.8%, the viscosity of 25 ° of 2,500 mPa-s and isolation HDI content was 0.3%, and the color number (car donor) of the light yellow transparent fluid and the isocyanate content was one or less.

[0029]1,000 g was taught for HDI, 0.4 g and 0.1g of ascorbic acid were taught to the same reactor as embodiment 2 Embodiment 1 for phenol, and nitrogen substitution of the inside of a reactor was carried out. The appearance of mixed liquor was in the state which ascorbic acid

distributed in the liquid which dissolved raw materials other than ascorbic acid. Next, 0.2g of THF solutions (10%) of potassium isovalerate were prepared, and the urethane-ized reaction and the isocyanuration reaction were performed in parallel at 50 °C for 5 hours. Then, 0.02g of phosphoric acid was added, it agitated with reaction temperature for 1 hour, and the reaction was stopped. Reaction liquid was filtered and ascorbic acid was removed. The isocyanate content of this liquid was 38.5%. Subsequently, thin film distillation was carried out at 160 °C and 13.3 Pa, unreacted HDI, phenol, and THF were removed, and the isocyanurate group content polyisocyanate P-2 was obtained. As for P-2, 23.2%, the viscosity of 25 °C of 1,500 mPa-s and isolation HDI content was 0.2%, and the color number (car donor) of the light yellow transparent fluid and the isocyanate content was one or less.

[0030] 3 g and 0.3g of ascorbic acid were taught [ HDI ] to the same reactor as embodiment 3 Embodiment 1 for 993 g and 1,3-BD, and nitrogen substitution of the inside of a reactor was carried out. The appearance of mixed liquor was in the state which ascorbic acid distributed in the liquid which dissolved raw materials other than ascorbic acid. Next, 0.2g of THF solutions (10%) of potassium isovalerate were prepared, and the urethane-ized reaction and the isocyanuration reaction were performed in parallel at 50 °C for 5 hours. Then, 0.02g of phosphoric acid was added, it agitated with reaction temperature for 1 hour, and the reaction was stopped. Reaction liquid was filtered and ascorbic acid was removed. The isocyanate content of this liquid was 32.5%. Subsequently, thin film distillation was carried out at 160 °C and 13.3 Pa, unreacted HDI/THF was removed, and the isocyanurate group content polyisocyanate P-3 was obtained. As for P-3, 20.5%, the viscosity of 25 °C of 2,700 mPa-s and isolation HDI content was 0.4%, and the color number (car donor) of the light yellow transparent fluid and the isocyanate content was one or less.

[0031] 1,000 g and 0.3g of ascorbic acid were taught to the same reactor as embodiment 4 Embodiment 1 for HDI, and nitrogen substitution of the inside of a reactor was carried out. The appearance of mixed liquor was in the state which ascorbic acid distributed in the liquid which dissolved raw materials other than ascorbic acid. Next, 0.2g of THF solutions (10%) of potassium isovalerate were prepared, and the urethane-ized reaction and the isocyanuration reaction were performed in parallel at 50 °C for 3 hours. Then, 0.02g of phosphoric acid was added, it agitated with reaction temperature for 1 hour, and the reaction was stopped. Reaction liquid was filtered and ascorbic acid was removed. The isocyanate content of this liquid was 39.0%. Subsequently, thin film distillation was carried out at 160 °C and 13.3 Pa, unreacted HDI/THF was removed, and the isocyanurate group content polyisocyanate P-4 was obtained. As for P-4, 23.5%, the viscosity of 25 °C of 1,400 mPa-s and isolation HDI content was 0.3%, and the color number (car donor) of the light yellow transparent fluid and the isocyanate content was one or less.

[0032] 3 g and 0.9g of phenol were taught [ HDI ] to the same reactor as comparative example

1 Embodiment 1 for 993 g and 1,3-BD, and nitrogen substitution of the inside of a reactor was carried out. The appearance of mixed liquor was a uniform solution. Next, 0.4g of THF solutions (10%) of potassium isovalerate were prepared, and the urethane-ized reaction and the isocyanuration reaction were performed in parallel at 50 °C for 16 hours. Then, 0.04g of phosphoric acid was added, it agitated with reaction temperature for 1 hour, and the reaction was stopped. The isocyanate content of this liquid was 32.7%. Subsequently, thin film distillation was carried out at 160 °C and 13.3 Pa, unreacted HDI, phenol, and THF were removed, and the isocyanurate group content polyisocyanate P-5 was obtained. As for the viscosity of 25 °C, P-5 was [ the light yellow transparent fluid and isocyanate content / the color number (car donor) of 2,300 mPa-s and isolation HDI content ] 1-2 0.3% 20.7%.

[0033]Raw material HDI used for Embodiments 1-4 and the comparative example 1 :

Hexamethylene-di-isocyanate 1,3-BD: 1,3-butanediol THF : Tetrahydrofuran [0034]- The color number was measured according to JIS K5400.

- The isolation HDI content was measured by gas chromatography.

- By FT-IR, the obtained polyisocyanate checked that the isocyanurate group was generating all.

[0035]

[Effect of the Invention]The manufacturing method of the isocyanurate group content polyisocyanate which was excellent in productivity was able to be provided by using ascorbic acid for a co-catalyst as explained above. The isocyanurate group content polyisocyanate obtained by this invention had little coloring.

[0036]The polyisocyanate obtained by this invention can be used for a coating material, adhesives, a coating agent, an elastomer, a modifier, form, a sealing material, etc.

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[Translation done.]